

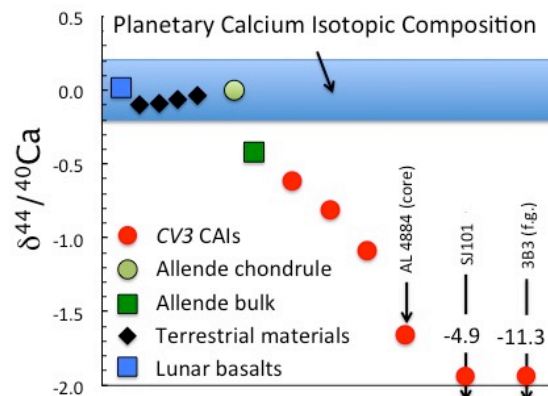
**CALCIUM AND TITANIUM ISOTOPE FRACTIONATION IN CAIS: TRACERS OF CONDENSATION AND INHERITANCE IN THE EARLY SOLAR PROTOPLANETARY DISK.** J. I. Simon<sup>1</sup>, M. K. Jordan<sup>2</sup>, M. J. Tappa<sup>1</sup>, I. E. Kohl<sup>2</sup>, and E. D. Young<sup>2</sup>. <sup>1</sup>Center for Isotope Cosmochemistry & Geochronology, Astromaterials Research and Exploration Science Division, NASA-Johnson Space Center, Houston, TX, USA. justin.i.simon@NASA.gov <sup>2</sup>Department of Earth, Planetary, and Space Sciences, UCLA, Los Angeles, CA, USA.

**Introduction:** The chemical and isotopic compositions of calcium-aluminum-rich inclusions (CAIs) can be used to understand the conditions present in the protoplanetary disk where they formed. The isotopic compositions of these early-formed nebular materials are largely controlled by chemical volatility. The isotopic effects of evaporation/sublimation, which are well explained by both theory and experimental work, lead to enrichments of the heavy isotopes that are often exhibited by the moderately refractory elements Mg and Si. Less well understood are the isotopic effects of condensation, which limits our ability to determine whether a CAI is a primary condensate and/or retains any evidence of its primordial formation history.

At issue is the degree to which the measured isotopic signatures of Ca and Ti compare to each other, to moderately refractory elements, and to theoretical models of fractionation. Our ability to assess whether CAIs are primary condensates from a homogenous solar gas or instead are melanges of heterogeneous presolar solids will place important constraints on the significance of these primitive solids.

Here we present new Ca ( $n=5$ ) and Ti ( $n=2$ ) isotope data from CV3 meteorites, including: Type A (Allende EK5-2-1), Type B1 (Allende AL4884 and Allende 461 “B”), reworked Type B (Northwest Africa, NWA 2364 “Crucible”), and fine-grained (Allende 3B3) inclusions. Additional Ca measurements were made for comparison purposes, including an Allende chondrule, terrestrial basalts and mineral standards, and lunar basalts (Fig. 1). Paired Ca and Ti data for AL4884 and “Crucible” along with data from the forsterite-bearing Type B (FoB) SJ101 inclusion [1,2] are compared to mass fractionation modeling for condensation [2-4].

**Sample Descriptions:** All of the studied CAIs, except for 461 “B” are large ( $> 5$  mm). Careful microdrilling afforded data from Allende Type B CAI 461 “B” and a complex chondrule that are  $\sim 500 \times 250 \mu\text{m}$  and  $300 \mu\text{m}^2$ , respectively. In general, the studied CAIs exhibit textures and mineralogy that are typical for their sub classifications. Exceptions include abundant “clots” of accessory refractory hibonite and perovskite ( $\pm$ spinel) within the melilite interior of Type A CAI EK5-2-1 [5] and the potentially reworked nature of Type B CAI “Crucible” [6].

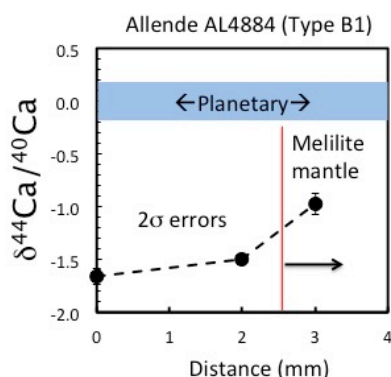


**Figure 1.** Ca isotopic compositions measured by double-spike TIMS methods for a suite of CV3 CAIs and other planetary materials. Bulk Allende data from [4] and CAI SJ101 data from [1]. Uncertainties are less than the size of the symbols used.

**Analytical Approaches:** Sample powders were obtained by microdrilling utilizing a New Wave Micro-Mill® system at NASA-JSC. Samples analyzed for Ca isotope compositions were dissolved in Parr digestion vessels, spiked, and fluxed 3x following procedures outlined in [7]. Ca purification was performed under vacuum with two steps of Eichrom TODGA resin chemistry outlined by [8]. Double spiked 42-48 Ca measurements are made using a Thermo Scientific TRITON mass spectrometer at NASA-JSC. The specific procedures including sample loading and analysis methodologies are similar, but improved on those of [4,8]. Mass dependent  $\delta^{40/44}\text{Ca}$  values reflect deviations from a “normal” planetary or chondritic composition [4]. Measured seawater, BCR-1 & 2, and SRM915a & b standards, as well as, melilite and augite terrestrial minerals (from the Smithsonian Institute) yielded their expected values. All samples were replicated with internal precisions that are less than the 0.13-0.18‰ (2 sd) long-term external reproducibility of the standards.

Ti analyses were conducted using laser ablation multiple-collector inductively coupled plasma-source mass spectrometry (LA-MC-ICPMS, ThermoFinnigan Neptune™) at UCLA. An outline of the method is described in [2]. Comparing the UCLA Glass #5 standard against pure  $\text{TiO}_2$  allows us to demonstrate the lack of matrix effects on  $\delta^{49/47}\text{Ti}$  within our current precision of  $\sim 0.15\text{-}0.2\text{‰}$  ( $1\sigma$ ).

**Analytical Results:** All studied CAIs have  $\delta^{40/44}\text{Ca}$  less than “normal”  $\sim 0\%$  planetary-like values [1,4]. Measured CAI values range from  $-0.6$  to  $-11.3\%$ , clearly resolved from the bulk Allende value [4] (Fig. 1). Type B’s “Crucible” and AL4884 were subsampled “*in situ*” by microdrilling. No resolvable difference was observed between the core and outer edge of “Crucible”,  $\delta^{40/44}\text{Ca} = -0.57 \pm 0.02\%$  ( $2\sigma$ ) and  $-0.66 \pm 0.14\%$  ( $2\sigma$ ), respectively. In contrast, a clear difference can be seen in AL4884, with the core yielding  $\delta^{40/44}\text{Ca} = -1.66 \pm 0.08\%$  ( $2\sigma$ ) and the melilite mantle yielding  $\delta^{40/44}\text{Ca} = -0.97 \pm 0.07\%$  ( $2\sigma$ ), Fig. 2. The Ti isotopic compositions of “Crucible” and AL4884 are similar and unresolvable from a chondritic value, i.e.,  $\delta^{49/47}\text{Ti} = 0.2 \pm 0.3\%$  ( $2\sigma$ ), see Fig. 3.



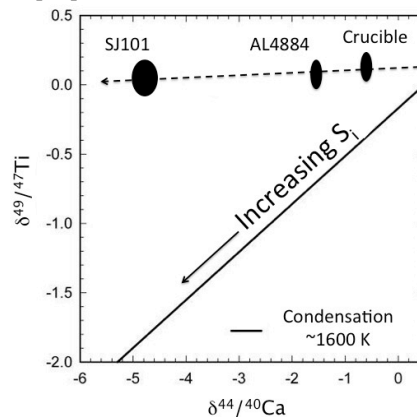
**Figure 2.** High precision evidence of intra-CAI Ca isotopic zoning. Relatively “heavy” melilite mantle (right) could reflect a changing reservoir effect during condensation or a boundary layer enrichment effect due to evaporation.

**Comparison to Condensation Models:** In [2] we considered the isotopic consequences of condensation from a nebular gas in terms of the kinetics of condensation, the degree of undercooling, and potential reservoir effects. Kinetic fractionation associated with condensation depends upon collisional frequency and the ability of a molecule to incorporate into the structure of the condensed phase [3,4]. Collisional frequency favors enrichment of lighter isotopes in the condensates.

The degree of saturation controls the relative contributions from equilibrium and kinetic isotope fractionation [4]. The saturation index  $S_i = P_i/P_{i,eq}$  quantifies the degree of saturation with  $S_i > 1$  implying condensation.  $S_i$  can be equated with a temperature difference from the equilibrium condensation temperature ( $T_{eq}$ ) using the Van’t Hoff equation and the enthalpy for the condensation reaction. Therefore,  $S_i$  corresponds to the degree of undercooling [4,9].

**Discussion and Future Work:** This multi-element isotopic work attests to the complicated formation histories of CAIs. This first report of intra-CAI Ca isotopic zoning implies that at least AL4884 condensed with isotopically light Ca compared to planetary materials and experienced later evaporation and/ or a changing

reservoir that significantly affected its surrounding melilite mantle. It is noteworthy that the sense of Ca zoning is inconsistent with typical Mg isotopic zoning profiles that often decrease from “heavy” in the interior to “normal” values at the edge, implying that Mg in CAIs is susceptible to later modification in the solid-state, cf. [10].



**Figure 3.** Correlation between  $\delta^{44/40}\text{Ca}$  and  $\delta^{49/47}\text{Ti}$  as a function of oversaturation ( $S_i$ ) calculated from the condensation model. Type B CAIs AL4884 (core), “Crucible”, and SJ101, plotted as filled  $2\sigma$  error ellipses, are possibly correlated, but trend off the theoretical curve.

The shallow trend in Fig. 3 implies that the Ca and Ti in these objects may not have experienced the same condensation history and that Ti, on the basis of persistent  $^{50}\text{Ti}$  anomalies, was inherited from a distinct reservoir. The presence of distinct reservoirs for these elements could be due to the fact that CAIs are aggregates of pre-existing materials as opposed to being original condensates. Alternatively, the shallow slope may indicate that a majority of the Ca and Ti condensed in response to different degrees of undercooling. This is possible because Ti has a higher  $T_{eq}$  than Ca by  $\sim 50^\circ\text{C}$  beyond their 50% condensation temperatures (at nebular pressures of  $10^{-5}$  bar, [11]). It would require differences in undercooling of just a few degrees [4]. In the latter case most Ti would have condensed near  $T_{eq}$  followed by undercooling where a majority of Ca and traces of remaining Ti condensed. Future comparisons between measurements and these self-consistent theoretical models for Mg, Si, Ca, and Ti isotope ratios will allow us to better understand the effects of condensation and the formation history of these objects.

**References:** [1] Huang S. et al. (2012) *GCA*, 77, 252-265. [2] Jordan M. et al. (2015) *LPSC*, Abst. #2472, [3] Young E.D. and Schauble E.A. (2012) *MetSoc*, Abst. #5382. [4] Simon J.I. and DePaolo D.J. (2010) *EPSL*, 289, 457-466. [5] Mishra R.K., et al. (2015) *MetSoc* Abst. #5133. [6] Friedrich J.M. et al. (2005) *LPSC* Abst. #1756. [7] Tappa, M. et al. (2015) *LPSC*, Abst. #2083. [8] Tappa M.J. et al. (2014) *LPSC* Abst. #1908. [9] Jouzel J. and Merlivat L. (1984) *JGR*, 89, 1749-1757. [10] Bullock E.S. et al., (2013) *MPS*, 48, 1440-1458. [11] Denton E. and Grossman L. (2000) *GCA*, 64, 339-366.